NOTES

TOHDITE (5Al$_2$O$_3$·H$_2$O) IN BAUXITES FROM NORTHERN AUSTRALIA

Tohdite (5Al$_2$O$_3$·H$_2$O), is a synthetic phase described by Yamaguchi *et al.* (1964a) having hexagonal symmetry (P6$_3$mc) with a = 5.58 Å and c = 8.77 Å. The structure of tohdite determined by Yamaguchi *et al.* (1964b) has four of the five aluminiums in octahedral coordination and the other in tetrahedral coordination, between four close-packed oxygen sheets (ABAC stacking). Shpanov *et al.* (1971) described akdalaite, a new mineral from a hydrothermal deposit, which they proposed was related to tohdite, but having a larger unit cell (a = 12.87 Å, c = 14.97 Å), slightly different composition (4Al$_2$O$_3$·H$_2$O), and minor amounts of Fe$_2$O$_3$, BeO, ZnO and MgO.

Bauxitic pisoliths are concentrically zoned pea-sized particles common in deeply weathered aluminous rocks, and are the main components of bauxite ore-bodies. From any one particular locality, individual pisoliths vary widely in concentric structure and mineral distribution. The mineral composition of pisoliths is dominated by gibbsite (Al(OH)$_3$) and boehmite (AlO(OH)), with variable minor quartz (SiO$_2$), hematite (Fe$_2$O$_3$), kaolinite (Al$_2$Si$_2$O$_5$(OH)$_4$) and anatase (TiO$_2$). Diaspore (AlO(OH)), goethite (FeO(OH)) and corundum (Al$_2$O$_3$) have also been reported from some bauxitic pisoliths. We report here evidence that tohdite constitutes an important component of some bauxitic pisoliths at Weipa, Cape York Peninsular, in northern Australia.

EXPERIMENTAL METHODS

The bulk of pisoliths from Weipa are somewhat porous and soft enough to powder from a light hammer tap. Some, however, have a porous rim and a hard vitreous core, requiring a sharp blow to crack them. Examination by X-ray diffraction of 42 pisoliths selected randomly from 16 drill holes showed that almost half contained more than 20 wt. % of a material not accounted for, by identifiable well-crystallized minerals, and yielding very broad diffraction maxima. We refer to this material as poorly-diffracting material (PDM). A few pisoliths contained more than 50 wt. % PDM. Pisoliths containing the highest percentage of poorly-diffracting material had a hard vitreous core surrounded by a softer porous rim. X-ray diffraction analysis of the vitreous core of such pisoliths was done

using a Siemens D501 X-ray diffractometer, Cu Kα radiation. Quantification of the mineralogy was determined on samples combined with 33.3 wt. % ZnO as an internal standard, using the software package SIRO-QUANT (Taylor and Clapp, 1992). Differential XRD patterns were obtained by slow-scanning the sample without the standard, followed by subtraction of the calculated pattern for each of the well-crystallized components in proportion to their weight fraction. The bulk chemical composition of the pisolith cores was established by energy dispersive X-ray analysis in a JEOL 6400 scanning electron microscope operating at 15 kV. Transmission electron microscopy of one sample was performed on a crushed sample on a carbon support film in a JEOL 200CX TEM. An infrared spectrum of the PDM was obtained using a Perkin-Elmer 1800 FTIR spectrophotometer.

RESULTS

The rim of vitreous-core pisoliths shows clear concentric zoning emphasized by a variation in Fe content. Zones having the highest Fe content appear bright in the back-scattered electron image (Figure 1). The core of such pisoliths displays no zonation. Quantitative
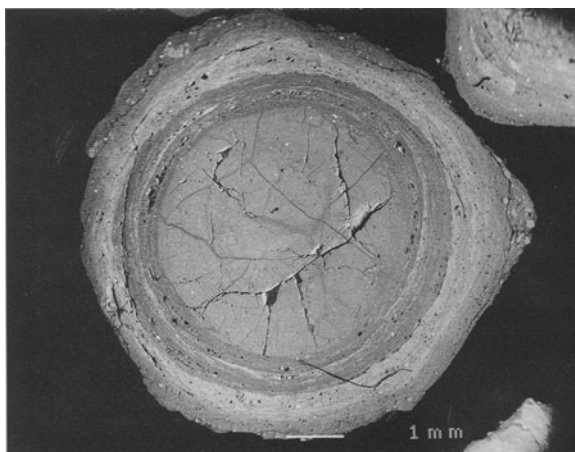

Figure 1. Back-scattered electron image of a vitreous-core pisolith displaying a concentrically banded rim and a fractured core devoid of zonation. Scale bar = 1 mm.

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Table 1. Quantitative XRD results from a vitreous-cored pisolith.

Phase	Weight % excluding PDM	Weight % including PDM
Gibbsite	31.47	5.06
Boehmite	0.06	0.01
Quartz	42.04	6.76
Hematite	6.34	1.02
Kaolinite	5.72	0.92
Anatase	14.37	2.31
PDM		83.92
Total	100.0	100.0

Table 2. Composition of bulk core material, crystalline components and composition of the poorly-diffracting material determined by difference.

	Bulk weight % (EDAX)	Crystalline minerals (SIROQUANT)	PDM composition
SiO_2	13.52	7.19	7.57
Al_2O_3	51.03	3.68	56.65
TiO_2	2.69	2.31	0.45
Fe_2O_3	2.64	1.02	1.94
H_2O	29.79*	1.88	33.39
PDM		83.92	
Total	99.67	100.0	100.0

* H_2O by difference.

XRD examination of the pisolith depicted in Figure 1 revealed that the core contained 84% poorly-diffracting material. Well-crystallized phases which yield sharp diffraction maxima included quartz, gibbsite, anatase, hematite, kaolinite and boehmite (Table 1).

TEM examination of the poorly-diffracting material revealed both structureless material and well-formed small crystals (6 nm diameter) with prominent 2.1 Å lattice fringes and less obvious fringes spaced at about
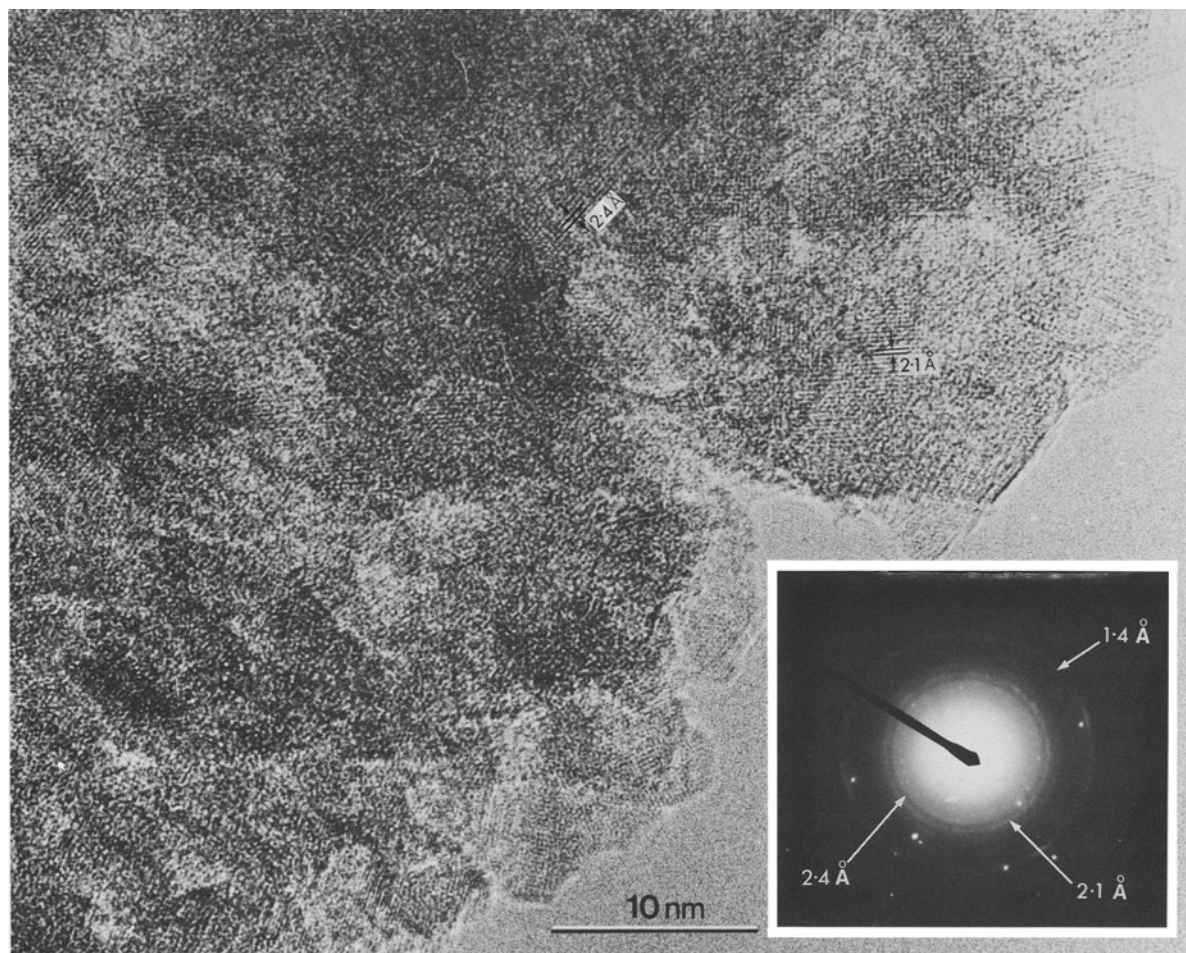

Figure 2. A TEM image of tohdite from Weipa bauxite showing small, well-formed crystals of 6 nm diameter and displaying prominent 2.1 Å lattice fringes and less obvious fringes spaced at 2.4 Å. The insert shows an electron diffraction pattern of the same material, displaying diffuse rings. The bright spots are associated with another well-crystallized phase. Scale bar = 10 nm.
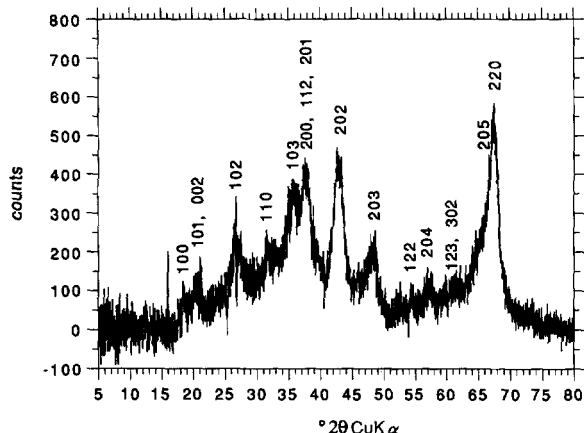
Figure 3. Differential XRD scan of tohdite from the core of a bauxitic pisolith. Broad peaks indicate extremely fine crystals of 7 nm diameter. The spike in the pattern at 16°2θ is due to an unaccounted minor phase. Spikes observed in the region between 25 and 28°2θ artifacts caused by the incomplete subtraction of the (101) quartz peak.

Table 3. XRD pattern for tohdite and differential XRD pattern of material from the core of a vitreous-core pisolith from Weipa.

hkl	Tohdite* d(Å)	I	Weipa d(Å)	I
100	4.85	10	4.81	20
002	4.38	23	4.38	25
101	4.23	11	4.23	15
			3.68	10
102	3.25	60	3.33	50
110	2.79	12	2.82	40
103	2.50	54	2.53	60
200	2.42	12		
112	2.35	77	2.37	65
201	2.33	38		
202	2.11	100	2.12	75
			1.97	5
203	1.86	48	1.89	40
			1.76	5
			1.72	5
122	1.69	13	1.69	20
204	1.62	26	1.61	25
123	1.55	34	1.55	20
302	1.51	20	1.52	25
205	1.42	68	1.41	55
220	1.39	85	1.39	100

* Yamaguchi et al. (1964b) (only tohdite lines of relative intensity > 10 are listed).

2.4 Å (Figure 2). The electron diffraction pattern from this material is: (relative intensity—d) 40—2.4 Å, 80—2.1 Å, 30—1.9 Å, 10—1.6 Å, 100—1.4 Å.

Table 2 shows the bulk composition of the core material, the calculated composition of the recognized well-crystallized minerals calculated from their ideal composition and weight percent (Table 1), and the composition of the poorly-diffracting material, established by difference.

A vitreous-core pisolith containing >90% PDM in its core was selected to produce a differential XRD scan as shown in Figure 3. Broad peaks are evident, their peak width at half maximum of 1.6°2θ indicates diffracting domains of the order of 7 nm. Relative intensity and d-spacing values are shown in Table 3, and compared with the results for tohdite described by Yamaguchi et al. (1964a). Although the breadth of the XRD peaks introduces overlap and makes accurate measurement of 2θ difficult, refinement of the cell parameters for Weipa tohdite using uniquely indexable reflections clear of interference from other components yields a = 5.555 Å and c = 8.968 Å, which are very close to those of synthetic tohdite.

A transmittance infrared spectrum of the material containing >90% PDM shows a broad absorption band at 3460 cm⁻¹ associated with O-H stretching vibrations (Figure 4).

DISCUSSION

The data presented here are consistent with the proposition that very fine-grained tohdite (or possibly akdalaite) is a major component of vitreous-cored pisoliths from Weipa, north Queensland. The differential XRD pattern provides the strongest evidence. The

slightly greater d-spacing values for the Weipa sample, particularly for hkl rather than 001 reflections, may be the result of lattice expansion from incorporation of Fe(III) in the Al sites; or be the result of displacement of peak maxima from the ideal Bragg position due to small crystal size effects. A chemical composition for Weipa tohdite cannot be established from the available data, as TEM and XRD evidence indicate other poorly-diffracting material may be present in the analyzed samples.

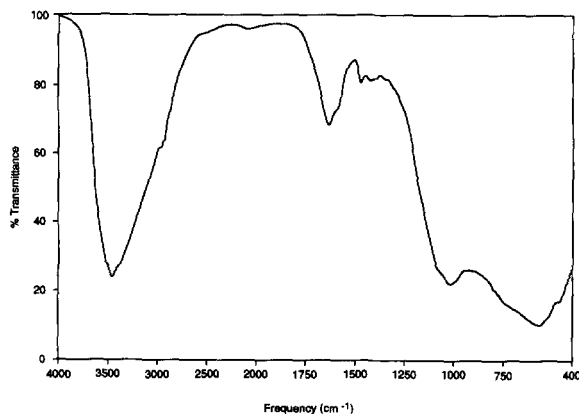The infrared spectrum of Weipa tohdite is dissimilar

Figure 4. A transmittance infrared spectrum of tohdite, showing a broad absorption band at 3460 cm⁻¹ associated with O-H stretching vibrations.

to well-crystallized gibbsite and boehmite. Between 2500 and 4000 cm^{-1}, the spectrum of gibbsite displays four absorption maxima associated with O-H stretching, whereas boehmite has two. The Weipa tohdite spectrum, on the other hand, has a broad absorption band with a maximum at 3460 cm^{-1} associated with the O-H stretching vibrational mode. Another maximum occurring at 1630 cm^{-1} is related to O-H bending. The infrared spectrum of Weipa tohdite is indicative of a material containing a large amount of strongly bound water. This may account for the discrepancy between the theoretical water content of tohdite and that determined chemically.

Tohdite (ideal composition 96.6 wt. % Al_2O_3) is the most aluminium-rich mineral recognized in the Weipa bauxite, and its presence is significant for both extraction of alumina from bauxite and in interpreting the origins of bauxitic pisoliths. While it is not possible to determine if the mineral at Weipa is indeed tohdite and not akdalaite, this is the first reported occurrence of tohdite/akdalaite in bauxites, and may, depending on the equivalence or non-equivalence of tohdite and akdalaite, be a new mineral occurrence.

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